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Michael J. Aziz

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1350 Massachusetts Avenue
Smith Center 600
Cambridge, MA 02138 -3846

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**14. ABSTRACT**
We performed experiments to test the hypothesis that partial counter-doping of sulfur-hyperdoped silicon would create a partially filled intermediate band, which could be used for sub-bandgap photodetection. We fabricated counter-doped Si:S:B of well-controlled crystal qual-ity and dopant concentration-depth profile, and we made three independent measurements of photoconductivity: one with contacts, and two without contacts. These measurements were per-formed in collaboration with the Persans group at RPI, the Buonassisi group at MIT, and the Warrender group at Bapát Labs. In all cases, the sub-bandgap photoresponse is negligibly small. We conclude from these

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**Report Title**

Deep Impurity Band Silicon for Subbandgap Photodetection


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Sub-bandgap photodetection using counter-doped silicon does not appear to be promising. The optoelectronic response appears to be less desirable than those of certain deep-level transi-tion metals in Si, which appear much more promising for future investigation.


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**Number of Papers published in non peer-reviewed journals:**

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**Number of Presentations:** 0.00

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## Technology Transfer

HARVARD SCHOOL OF ENGINEERING AND APPLIED SCIENCES

# DEEP IMPURITY BAND SILICON FOR SUBBANDGAP PHOTODETECTION

**Final Report** submitted to the Army Research Office
Short Term Innovative Research Program
W911NF-12-1-0196
Research Area 6.3: Sensors and Detectors
Program Officer: William W. Clark

P.I.: Michael J. Aziz, Harvard School of Engineering and Applied Sciences, Cambridge MA 02138

Submission date: March 12, 2013

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# DEEP IMPURITY BAND SILICON FOR SUBBANDGAP PHOTODETECTION

**Abstract**

We performed experiments to test the hypothesis that partial counter-doping of sulfur-hyperdoped silicon would create a partially filled intermediate band, which could be used for sub-bandgap photodetection. We fabricated counter-doped Si:S:B of well-controlled crystal quality and dopant concentration-depth profile, and we made three independent measurements of photoconductivity: one with contacts, and two without contacts. These measurements were performed in collaboration with the Persans group at RPI, the Buonassisi group at MIT, and the Warrender group at Benét Labs. In all cases, the sub-bandgap photoresponse is negligibly small. We conclude from these results that the lifetime of photo-excited carriers is very small -- less than about 10 ns.

Sub-bandgap photodetection using counter-doped silicon does not appear to be promising. The optoelectronic response appears to be less desirable than those of certain deep-level transition metals in Si, which appear much more promising for future investigation.

**Background**

Our prior research had demonstrated an insulator-to-metal transition in silicon hyperdoped with sulfur or selenium when the chalcogen concentration exceeded a critical value of about 0.7 at.%. Density functional theory indicates that the chalcogen creates a deep level in the silicon band gap and that increasing the chalcogen concentration turns this deep level into an impurity band, as shown in Fig. 1, which is completely filled.

Our hypothesis was that partial counter-doping with an acceptor, such as boron, would lead to a partially filled impurity band which could be exploited for sub-bandgap photodetecction. Consequently, the statement of work for this project was:

(1) Fabricate pn junction photodiodes from silicon hyperdoped with sulfur and partially compensated with boron using ion implantation and nanosecond pulsed laser melting.

(2) Measure responsivity in reverse bias over spectral range 900-2000 nm.

**Procedures and Results**

Si(001) samples were all implanted with sulfur to a dose of 3e15/cm$^2$ at 95 keV, giving an average range of 119 nm. Boron was implanted into these samples at 25 keV to doses of 3e13, 1e14, 3e14, 1e15, and 3e15 /cm$^2$.

Pulsed laser melting (PLM) was carried out using a 308 nm XeCl excimer laser producing a pulse with FWHM of ~25 ns and fluences between 1.7-1.8 J/cm$^2$. The melt duration was measured using transient reflectivity, with a 408 nm Ar-ion laser at 200 mW and a fast (ns-resolution) photodiode. These melt durations were then compared with simulated durations produced by a numerical solution of the 1-

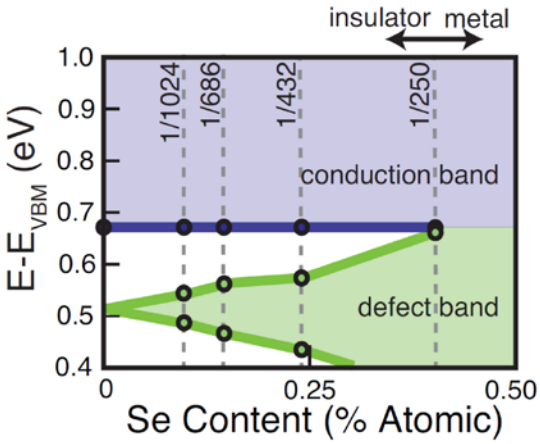


**Fig. 1:** *Ab initio* calculations of band structure of silicon hyperdoped with selenium, from [1]. Filled defect band broadens until it intersects conduction band at 0.4% Se causing insulator-to-metal transition.

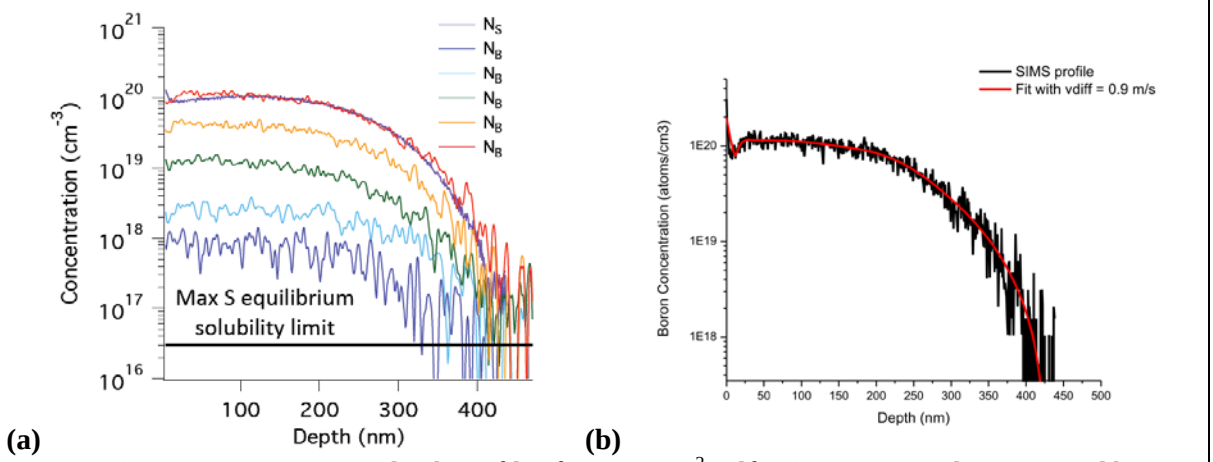


**Fig. 2:** (a) SIMS concentration depth profiles for 3e15/cm$^2$ sulfur (topmost purple curve) and boron of various doses (bottom to top: 3e13, 1e14, 3e14, 1e15, and 3e15 /cm$^2$) after ion implantation and PLM. (b) Comparison of highest boron dose to simulation of melting, rapid solidification, and solute trapping with diffusive speed $v_{diff}$ = 0.9 m/s.

D heat equation to determine melt depth and to calibrate fluence of the pulse.

SIMS depth profiles of dopant distributions are shown in Fig. 2(a). The topmost purple curve in the plot shows the sulfur profile, which was the same for all samples with varying amounts of boron compensation. The plot also shows the boron profiles for 5 different boron doses with various degrees of compensation, illustrating how well matched are the boron and sulfur concentration depth profiles. Dopant profile evolution during PLM was modeled using a 1-D finite element model of solute diffusion during pulsed-laser melting to determine the diffusive velocity, $v_{diff}$, characterizing the incorporation of boron in silicon during rapid solidification. A $v_{diff}$ value of 0.9 m/s gave the best fit to the data, as seen in Fig. 2(b). The ability to measure this diffusive velocity gives us the ability to accurately predict the dopant profile that will result from future implantation and PLM processes. Combined with prior results on sulfur, the Sulfur + Boron hyperdoped system can now be tuned to produce a wide range of desired counter-doping conditions.

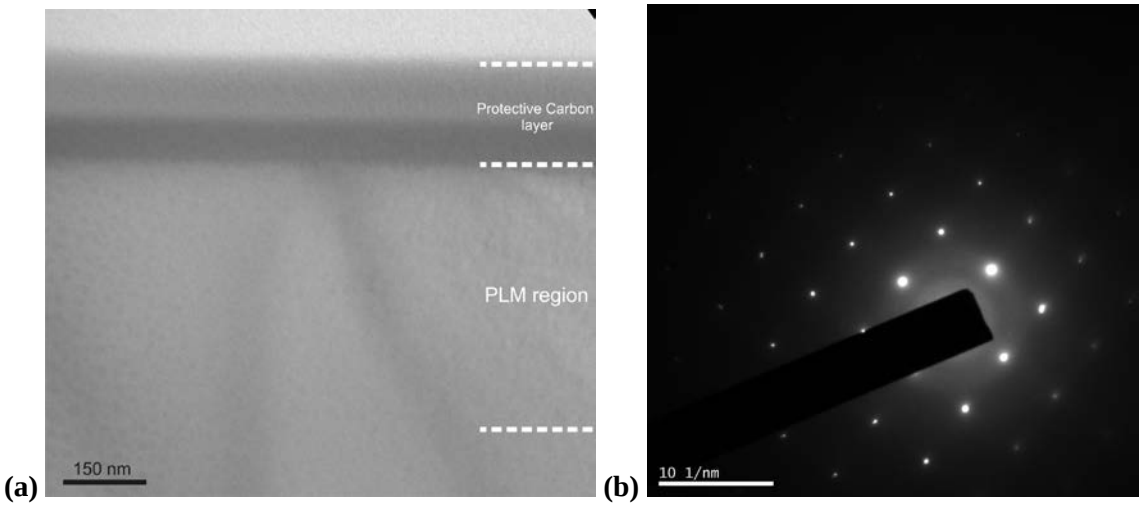


**Fig. 3:** (a) XTEM micrograph of highest boron-dose sample showing defect-free single crystal device layer. (b) Electron diffraction pattern confirming single crystal.

Cross-sectional TEM samples were prepared via Focused-Ion Beam (FIB) liftout and polishing on a Zeiss NanoVision Dual-Beam FIB; a protective layer of carbon was deposited on the samples prior to FIB milling, to prevent ion implantation and amorphization by Ga ions at 30 keV. Samples were imaged on a JEOL 2100 HRTEM at 200 keV. All implanted and PLM-processed samples of (001) oriented material were found to have no extended defects or precipitates present in the PLM region (see Fig. 3). Electron diffraction confirmed that this area was indeed single-crystal silicon.

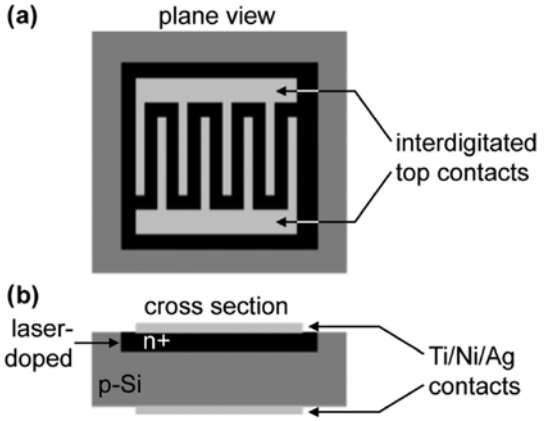


**Fig. 4:** (a) Top view and (b) cross section of sulfur-hyperdoped silicon photodiode exhibiting gain and extended NIR photoresponse out to 1200 nm [2].

**Photoconductivity measurements**

Fig. 5(a) shows a schematic of the experimental setup and the data acquired for a room temperature measurement of photoconductivity at different wavelengths for a counter-doped sample that was implanted with 3e15/cm$^2$ of sulfur and 1e15/cm$^2$ boron. With a dopant ratio of B/S = 33%, this sample should have a partially occupied band of states within the silicon band gap, although we have no proof that these states are delocalized.

To measure the photoconductivity, two contacts of a Ti/Ni/Ag stack were deposited on the surface of the PLM region, in collaboration with Christie Simmons and Tonio Buonassisi (MIT). These contacts were then wire-bonded to electrodes and the resulting device was incorporated into the circuit shown above. The circuit was custom designed and built to optimize the measured photoconductive signal from the sample. The circuit is a Wheatstone bridge design with the sample as one of the legs of the circuit. A Keithley 2425 source meter was used for the voltage supply, $V_S$, and a Signal Recovery 7265 Lock-In was used to measure the voltage, $V_M$. A Princeton Instruments white light source and Acton SP2150i monochrometer were used to supply a tunable monochromatic light source which was then chopped at 83 Hz using a ThorLabs

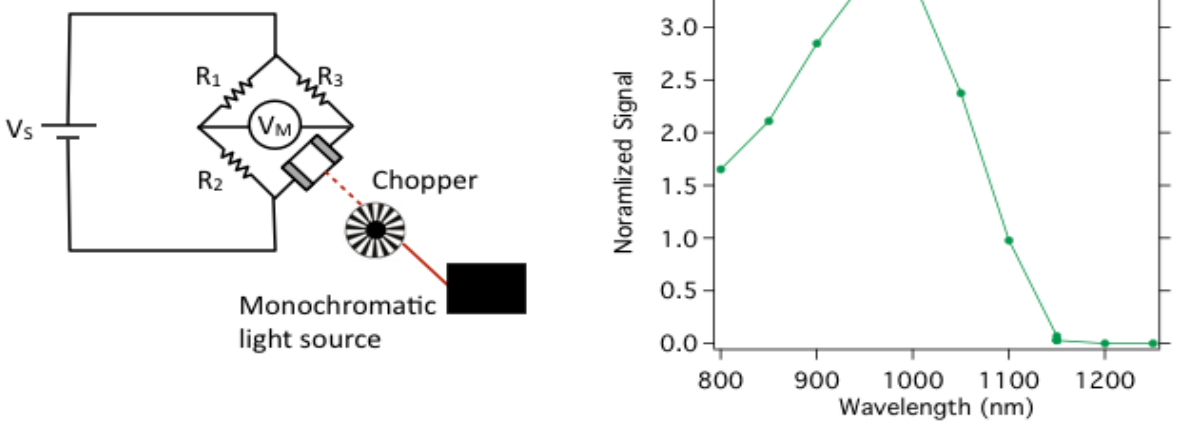


**Fig. 5:** (a). Wheatstone bridge setup for measuring small photoconductivity effect. (b) Spectral response for counter-doped sample with a dopant ratio of B/S = 33%.

MC2000 Optical Chopper System before shining onto the device.

Fig. 5(b) shows the Normalized Signal = $V_M$ / $V_S$ vs. wavelength, where $V_M$ is the measured voltage. We measured a strong photoconductive response for photon energies above the silicon band gap, but we were unable to detect any response below the silicon band gap. We believe that the reason for this is that the generation rate from our monochromatic light source is not high enough to compensate for the low lifetimes in this material. The maximum optical power we could get was 0.2 mW at 1000 nm (this peak in output power is why the normalized signal above peaks at this wavelength), and this is focused to a spot size of about 1 mm. Next we moved on to brighter light sources.

**Microwave reflectivity during chopped laser diode pumping**

PLMed samples were interrogated using microwave reflectivity to measure change in carrier concentration under illumination with above- and below-gap light. Measurements were carried out at Benét Laboratories at the Watervliet Arsenal in Watervliet, NY, with the assistance of Drs. Jeffrey Warrender and Jay Mathews. Professor Peter Persans of RPI, and his student David Hutchinson, provided assistance and consultation. Samples were illuminated with chopped light from laser diodes at 405, 980, and 1550 nm. Changes in the microwave reflectivity of the samples, a direct measurement of photoconductive response, were observed for 405 and 980 nm light, but the magnitude of the response was equal to or slightly less than that of a reference sample of virgin crystalline silicon. No response was measured for 1550 nm light on any of the samples, suggesting a very short (< 10 ns) carrier lifetime in these materials.

**Microwave reflectivity during OPO laser pumping**

In collaboration with David Hutchinson (RPI) and Jay Mathews (Benét Laboratories), and Christie Simmons and Tonio Buonassisi (MIT), we performed a contactless microwave measurement of photoconductivity as we did in [3]. This measurement is particularly useful because it eliminates the possibly of false signal resulting from electrical contacts. We used an Ekspla 342B-10-W400 tunable ns pulsed laser system to optically pump the sample, and measured the resulting change in the microwave reflectivity of the sample due to photogenerated carriers. The pulsed laser system can output a few mJ of optical power, has a pulse duration of 6 ns FWHM,

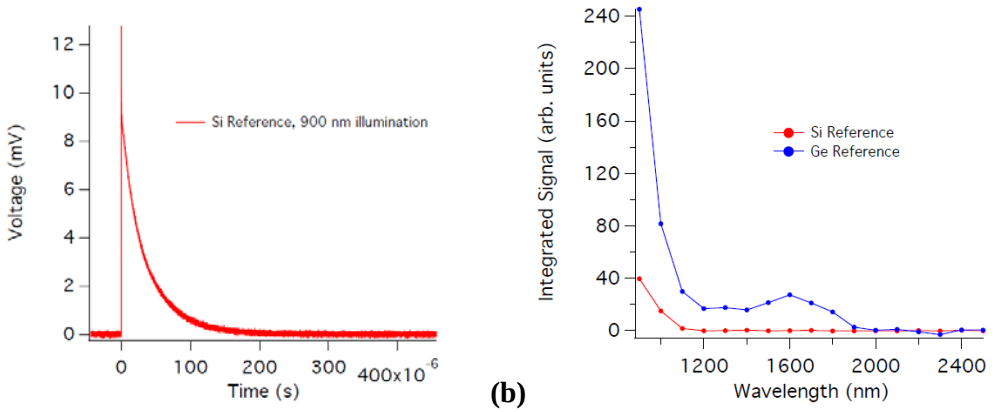


**Fig. 6:** (a). Temporal microwave reflectivity response of Si reference to 6 ns pulse at 900 nm. (b) Spectral response of reference samples of Si (red) and Ge (blue).

and the wavelength is tunable over the range of interest. We tested the system using both a plain Si and plain Ge reference. Fig. 6(a) shows the time-resolved response of the silicon reference when pumped with 900 nm illumination, and Fig. 6(b) shows the integrated signal for the Si and Ge reference as a function of wavelength. The wavelength dependence of the photoconductive response for the two reference materials is as expected based on their respective band gaps and absorption coefficients.

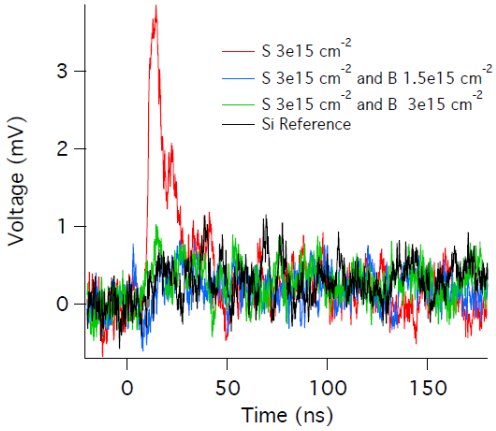


**Fig. 7:** Temporal microwave reflectivity response to 1500 nm wavelength OPO pump. Counter-doped samples (blue and green) are less responsive than plain sulfur-doped sample (red).

The counter-doped silicon samples were less responsive than the plain sulfur-doped sample, which itself was not very responsive. To see any time-resolved signal at all, we had to amplify the signal by 40 dB. Fig. 7 shows the response measured with 1500 nm wavelength pump illumination on 4 samples: a silicon reference, a hyperdoped silicon sample with only sulfur, and two counter-doped samples, with the B/S ratios of 50% and 100%. We detected a very small signal in the sulfur only sample, with a decay of only ~10 ns, but we measured no signal above the noise for the counter-doped samples. Our working hypothesis is that the lifetime in the counter-doped samples is shorter than in the sulfur only sample, resulting in no measurable photoconductive signal.

Although we have not yet published any results from this study, we plan to analyze these results more thoroughly in order to establish a more precise upper limit on the photocarrier lifetime, and to submit them for publication.

**Conclusions**

We have fabricated counter-doped Si:S:B of well-controlled crystal quality and dopant concentration-depth profile, and we have made three independent measurements of photoconductivity: one with contacts, and two without contacts. In all cases, the sub-bandgap photoresponse is negligibly small. We conclude from these results that the lifetime of photo-excited carriers is very small -- less than about 10 ns. We are working on a more precise evaluation of the carrier lifetime.

Sub-bandgap photodetection using counter-doped silicon does not appear to be promising. The optoelectronic response appears to be less desirable than those of certain deep-level transition metals in Si, which appear much more promising for future investigation.

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